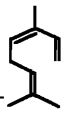
IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO3_VOC39

This data sheet last evaluated: June 2013; last change in preferred values: June 2013.



NO_3 + (ocimene, cis and trans) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(2.23 \pm 0.06) \times 10^{-11}$	294	Atkinson et al., 1985	RR (a)

Ocimene is 3,7-dimethyl-1,3,6-octatriene.

Comments

(a) 4000 L Teflon chamber at 294 K and 980 mbar (735 Torr) of air. NO_3 was generated by the thermal decomposition of N_2O_5. Ocimene and 2-methyl-2-butene were monitored by GC. Correction made to the ocimene loss rate due to reaction with NO_2 was < 12 %. The rate constant ratio, $k(NO_3$ + ocimene) / $k(NO_3$ + 2-methyl-2-butene) = 2.38 ± 0.06 is placed on an absolute basis by $k(NO_3$ + 2-methyl-2-butene) = 9.37 x 10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson and Arey, 2003). The rate constants for the cis and trans-isomers of ocimene were found to be (within 8 %) identical.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	2.2 x 10^{-11}	298
Reliability		
$\Delta \log k$	± 0.15	298

Comments on Preferred Values

The preferred value of the room temperature rate coefficient is based on the single study of Atkinson et al. (1985). The error limits are expanded to reflect the necessity to correct for removal of ocimene by reaction with NO_2 and because the results have not been confirmed.

There are no product studies of this reaction, though the large rate constant indicates that the reaction proceeds mainly via addition of NO_3 across a double bond to form a chemically activated nitrooxyalkyl radical. At pressures found in the troposphere this adduct will undergo collisional stabilization prior to reaction with O_2 to form a nitrooxyalkyl peroxy radical or

decompose to release NO_2. At atmospheric pressure the formation of the peroxy radical will generally dominate.

References

Atkinson, R., Aschmann, S. M., Winer, A. M., and Pitts, J. N., Env. Sci. Tech., 19, 159-163, 1985.
Atkinson, R., and Arey, J., Chem. Rev., 103, 4605-4638, 2003.